

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
11 December 2003 (11.12.2003)

PCT

(10) International Publication Number  
**WO 03/102071 A1**

(51) International Patent Classification<sup>7</sup>: **C08K 7/00,**  
H01L 23/373, C08L 83/04

(21) International Application Number: **PCT/JP03/06798**

(22) International Filing Date: **29 May 2003 (29.05.2003)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:  
2002-158434 **31 May 2002 (31.05.2002) JP**

(71) Applicant (*for all designated States except US*): **DOW CORNING TORAY SILICONE CO., LTD.** [JP/JP]; 1-3, Marunouchi 1-chome, Chiyoda-ku, Tokyo 100-0005 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **YAMAKAWA, Kimio** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusaigaigan, Ichihara-shi, Chiba 299-0108 (JP). **NAKAYOSHI, Kazumi** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusaigaigan, Ichihara-shi, Chiba 299-0108 (JP). **ISHIKAWA, Hiroki** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division,

2-2, Chigusaigaigan, Ichihara-shi, Chiba 299-0108 (JP). **MINE, Katsutoshi** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusaigaigan, Ichihara-shi, Chiba 299-0108 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: THERMOCONDUCTIVE CURABLE LIQUID POLYMER COMPOSITION AND SEMICONDUCTOR DEVICE PRODUCED WITH THE USE OF THIS COMPOSITION

(57) Abstract: A thermoconductive curable liquid polymer composition includes (A) a curable liquid polymer, (B) a filler made from a thermally-elongatable shape-memory alloy, and (C) a thermoconductive filler other than (B). A semiconductor device has a semiconductor element glued or coated with the thermoconductive curable liquid polymer composition.

WO 03/102071 A1

**[0001]** This invention relates to a thermoconductive curable liquid polymer composition and a semiconductor device manufactured with the composition. More specifically, the invention relates to a thermoconductive curable liquid polymer composition, which prior to curing possesses good flowability and after curing produces a cured body of excellent thermal conductivity. The invention further relates to a semiconductor device that demonstrates high reliability provided by coating or by adhesively connecting semiconductor elements with the composition.

**[0002]** Curable liquid compositions that contain thermoconductive fillers find application in the manufacture of electrical and electronic devices as heat-radiating adhesives, potting agents, or protective coatings. In particular, a curable liquid silicone composition comprising a liquid organopolysiloxane with at least two alkenyl groups in one molecule, a liquid organopolysiloxane with at least two silicon-bonded hydrogen atoms in one molecule, a hydrosilylation reaction metal catalyst, and a thermoconductive filler is suitable for forming cured bodies of low internal stress and excellent thermal conductivity. Therefore, this composition finds application in the manufacture of heat-removing adhesives placed between the semiconductor elements and heat-dissipation fins, as well as in the production of protective coating agents, potting agents, and heat-removing adhesives used in electric and electronic parts and devices.

1

5

## OBJECTS OF THE INVENTION

[0004] It has been found that flowability prior to curing and thermal conductivity after curing can be achieved by combining a thermoconductive filler with a thermally-elongatable shape memory alloy in the composition. Therefore, it is an object of this invention to provide a thermoconductive curable liquid polymer composition, which prior to curing possesses flowability and after curing produces a cured body of excellent thermal conductivity. A further object is to provide a semiconductor device that demonstrates high reliability provided by coating or by adhesively connecting semiconductor elements with the composition.

## SUMMARY OF THE INVENTION

[0005] A thermoconductive curable liquid polymer composition of this invention comprises: (A) a curable liquid polymer; (B) a filler made from a thermally-elongatable shape-memory alloy; and (C) a thermoconductive filler other than component (B). A semiconductor device of the invention has semiconductor elements that are glued or coated with the thermoconductive curable liquid polymer composition.

20

## BRIEF DESCRIPTION OF THE DRAWINGS

[0006] Figure 1 is a cross-sectional view of an LSI shown in the form of a semiconductor device of this invention.

- 1 semiconductor element
- 2 circuit substrate
- 25 3 circuit pattern element
- 4 bonding wire
- 5 thermoconductive curable liquid polymer composition
- 6 heat-dissipation fins

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

30 [0007] A curable liquid polymer of component (A) may comprise a thermosetting liquid polymer, room-temperature-curable liquid polymer, moisture-curable liquid polymer, ultraviolet-ray-curable liquid polymer, electron-beam-curable liquid polymer, etc. Among these, the most preferable is a thermosetting liquid polymer. If component (A) does not possess thermosetting properties, then, in order to cause elongation of component (B) prior to curing, during curing, or after curing, it is necessary to increase the temperature above the transition point of the shape memory

5 alloy filler, which constitutes component (B). The following are examples suitable for use as component (A): a curable liquid epoxy resin, curable liquid silicone, curable liquid polyimide resin, curable liquid phenol resin, curable liquid polyphenylenesulfide resin, curable liquid unsaturated polyester resin, curable liquid polyurethane resin, and a curable liquid diallylphthalate resin. Most preferable among the above are a curable  
10 liquid epoxy resin or a curable liquid silicone, which, when cured, acquires a rubber-like or a gel-like state. The curable liquid epoxy resin may be of a bisphenol type, biphenyl type, novolac type, etc., and is normally used in combination with a curing agent. The curable liquid silicone may be represented by a liquid silicone composition curable by means of an addition reaction, a liquid silicone composition curable in a reaction  
15 promoted with the use of a peroxide compound, a liquid silicone composition curable by means of a condensation reaction, a liquid silicone composition curable under the effect of ultraviolet rays, and a radiation-curable liquid silicone composition. The most preferable of the above is a liquid silicone composition curable by means of an addition reaction. It is recommended to use component (A) in the composition of the  
20 invention in an amount of 2.0 to 70 wt.%, preferably 5.0 to 50 wt.%.  
[0008] Component (B) is a filler. Component (B) is made from a thermally-elongatable shape memory alloy which elongates after heating to a temperature exceeding its transition point. Component (B) significantly improves thermal conductivity of the composition. This makes it possible to reduce the content of  
25 component (C). The filler of component (B) can be represented by a shape memory alloy of a Ti-Ni type, Cu-Zn-Al type, Cu-Al-Ni type, or the like. This alloy may be used in the form of fibers, scales, flakes or plates. The fiber shape is preferable. It is recommended that the diameter of the fiber shaped particles be 5 to 500 micrometers ( $\mu\text{m}$ ), preferably 10 to 300  $\mu\text{m}$ . It is recommended that the average particle diameter  
30 of the scale or flake or plate shaped particles be 5 to 500 micrometers ( $\mu\text{m}$ ), preferably 10 to 300  $\mu\text{m}$ . The filler particles may have a coil (helical) shape, a ring shape, or a curl shape. In the case of coil-shaped particles, it is recommended that their core diameter be 0.01 to 5.0 millimeters (mm), preferably 0.1 to 1.0 mm. It is recommended that the normal length of the particles be 10  $\mu\text{m}$  to 10 mm, preferably 20  $\mu\text{m}$  to 2 mm.  
35 It is recommended that the length after elongation be 0.1 to 50 mm, preferably from 0.2 to 10 mm. It is recommended that heating allows 2 to 50-fold, preferably 3 to 15-fold

5 increase in the length of the component (B). The surface of component (B) can be treated with an organohalosilane, organoalkoxysilane, organosilazane, or a similar organic silicon compound. The aforementioned shape-memory alloy fillers can be used in a combination. It is recommended to use component (B) in the composition of the invention in an amount of 0.01 to 30 wt.%, preferably in an amount of 0.1 to 20  
10 wt.%.

[0009] There are no special limitations with regard to the type of thermoconductive filler (C), except that it should not be the same as component (B). For example, component (C) can be silica, alumina, glass, silicate, silicon nitride, boron nitride, aluminum nitride, silicon carbide, titanium oxide, carbon black, diamond, or a similar  
15 inorganic-type filler; aluminium, aluminium hydroxide, aluminum sulfide, gold, silver, copper, nickel, solder, brass, palladium, or a similar metal-type filler; an organic resin filler containing the aforementioned fillers; or mixtures of the above. Among the above, the inorganic fillers and metal fillers have the best thermal conductivity. It is recommended that particles of component (C) have diameters of 0.1 to 500  $\mu\text{m}$ ,  
20 preferably 0.1 to 100  $\mu\text{m}$ . Particles of component (C) can be surface-treated with an organohalosilane, organoalkoxysilane, organosilazane, or a similar organic silicon compound. The aforementioned thermoconductive fillers can be used in a combination. It is recommended to use component (C) in the composition of the invention in an amount of 30 to 98 wt.%, preferably from 50 to 95 wt.%.

25 [0010] At room temperature, the composition of the invention is liquid. More specifically, at 25°C, the composition may have viscosity of 0.1 to 100,000 Pascal-seconds (Pa·s), preferably 0.5 to 50,000 Pa·s, more preferably 0.5 to 10,000 Pa·s. There are no special restrictions with regard to hardness after curing, and the product may be produced in the form of resin, rubber, or gel, or it may be produced as a  
30 partially-cross-linked, i.e, semi-cured rubber or gel. It is advantageous to cure the composition of the invention into a soft, semi-cured gel when it is used to form an adhesive or a coating for a semiconductor device. In this case, it is recommended that the hardness of a cured product measured in accordance with JIS K6253 is less than 10, and preferably is equal to 0. As viscosity and flowability of the composition of the  
35 invention will vary depending on viscosity of component (A), as well as on the shape

5 and size of component (B) and on the shape and size of component (C), the components of the composition should be proportioned so as to provide an appropriate flowability.

[0011] When component (A) is a curable liquid silicone, a thermoconductive addition-reaction-curable liquid silicone composition preferably having a viscosity of 0.1 to 300 Pa·s at 25°C may be prepared from the following components:

- 10 (a) 100 parts by weight of a liquid organopolysiloxane having at least two alkenyl groups per molecule;
- (b) 0.001 to 100 parts by weight of a liquid organopolysiloxane having at least two silicon-bonded hydrogen atoms per molecule;
- (c) hydrosilylation-reaction metal catalyst used in such an amount that in terms of
- 15 weight units the content of metal atoms in the catalyst is 0.01 to 1,000 parts per million (ppm) based on the total weight of the composition;
- (B) a filler made from a thermally-elongatable shape memory alloy; and
- (C) a thermoconductive filler other than component (B).

[0012] Aforementioned component (a) is characterized by having at least two

20 silicon-bonded alkenyl groups per molecule. Structurally this component may have a linear chain, a partially-branched linear chain, a branched chain, a cyclic, or a net-like structure. The linear-chain structure is preferable. The following are examples of suitable alkenyl groups: vinyl group, allyl group, and hexenyl group. Bonding positions of the alkenyl group may be at the molecular terminals and/or along the side

25 molecular chain. Positions at both molecular terminals are preferable. The silicon-bonded groups other than the alkenyl group may be the following substituted or unsubstituted monovalent hydrocarbon groups: methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, or similar alkyl group; phenyl group, tolyl group, xylyl group, naphthyl group, or a similar aryl group; benzyl

30 group, phenethyl group, or a similar aralkyl group; chloromethyl group, 3-chloropropyl group, 3,3,3-trifluoropropyl group, or a similar halogenated alkyl group. The most preferable among the above are methyl and phenyl groups. It is recommended that the viscosity of component(a) be 10 to 1,000,000 milliPascal-seconds (mPa·s) at 25°C, preferably 100 to 50,000 mPa·s. If the viscosity of component (a) is below 10 mPa·s,

35 it would be difficult to provide sufficient mechanical strength after curing. If the

5 viscosity of component (a) exceeds 1,000,000 mPa·s, the composition would be difficult to handle because it becomes too viscous.

[0013] Component (b) contains at least two silicon-bonded hydrogen atoms per molecule. Component (b) may comprise a cross-linking agent or the curing agent of component (a). Therefore, when component (a) contains two alkenyl groups, the  
10 number of silicon-bonded hydrogen atoms should be three or more. Component (b) may have a linear, partially-branched linear, branched, or a net-like molecular structure. A bonding position of the silicon-bonded hydrogen atom may be at the molecular terminals and/or along the side molecular chain. The silicon-bonded groups other than the silicon-bonded hydrogen may be the following substituted or unsubstituted  
15 monovalent hydrocarbon groups: methyl group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group, or a similar alkyl group; phenyl group, tolyl group, xylyl group, naphthyl group, or a similar aryl group; benzyl group, phenethyl group, or a similar aralkyl group; chloromethyl group, 3-chloropropyl group, 3,3,3-trifluoropropyl group, or a similar halogenated alkyl group. The most preferable  
20 among the above are methyl and phenyl groups. It is recommended that the viscosity of component(b) be 0.1 to 1,000,000 mPa·s at 25°C, preferably from 0.2 to 10,000 mPa·s. It is recommended to use component (b) in an amount of 0.001 to 100 parts by weight, preferably from 0.001 to 30 parts by weight, for each 100 parts by weight of component (a). If component (b) is used in an amount less than 0.001 parts by weight, it  
25 would be difficult to completely cure the composition. If the content of component (b) exceeds 100 parts by weight, it would be difficult to obtain a cured body of sufficient physical strength. To cure the composition to a sufficient degree, it is recommended that alkenyl groups of component (a) be present in an amount of 0.1 to 10 moles, preferably 0.5 to 5 moles, for each 1 mole of the silicon-bonded hydrogen atoms of  
30 component (b). If the aforementioned alkenyl groups are in an amount less than 0.1 mole, it would be difficult to ensure sufficient curing. If the alkenyl groups exist in an amount exceeding 10 moles, the cured body will be produced with reduced physical strength.

[0014] Component (c) is a catalyst for the addition reaction of the silicon-bonded  
35 hydrogen atoms of component (b) to the alkenyl groups of component (a). Component (c) may comprise a platinum-type catalyst, rhodium-type catalyst, or a palladium-type

5 catalyst. The platinum catalyst is the most preferable. The following are specific examples of the aforementioned catalysts: a platinum powder, platinum black, platinum on a fine silica powder carrier, platinum on an activated carbon carrier, a chloroplatinic acid, an alcoholic solution of a chloroplatinic acid, a platinum-olefin complex, a platinum-alkenylsiloxane complex, or a similar platinum-type catalyst. It is  
10 recommended to add component (c) in such an amount that, in terms of weight units, the content of metal atoms in component (c) is 0.01 to 1,000 ppm, preferably 0.01 to 100 ppm in the composition of the invention. If the aforementioned content is below 0.01 ppm, the addition reaction would not properly progress and it would be difficult to ensure sufficient curing. If the content of component (c) exceeds 1,000 ppm, it would  
15 not noticeably further promote the addition reaction, but would make the cost of the composition economically unjustifiable.

[0015] A filler (B) made from a thermally-elongatable shape-memory alloy and a thermoconductive filler (C), other than the aforementioned filler (B), are the same as defined above. It is recommended to use component (B) in the amount of 1 to 1,000  
20 parts by weight, preferably in the amount of 1 to 500 parts by weight for each 100 parts by weight of component (a). It is recommended to use component (C) in the amount of 50 to 5,000 parts by weight, preferably in the amount of 100 to 3,000 parts by weight for each 100 parts by weight of component (a).

[0016] The thermoconductive liquid silicone composition curable by means of an  
25 addition reaction is prepared from the components described above. However, other components can be added. These additional components include the following: shape memory resin, silicone resin, fluoro resin, or a similar fine organic resin powder, as well as dyes, pigments, flame retardants, solvents, etc. The shape memory resin can be exemplified by a vinyl-type polymer, olefin-type polymer, acryl-type polymer,  
30 caprolactone-type polymer, ester-type polymer, urethane-type polymer, or compounds prepared from the aforementioned organic resins and the shape-memory alloys.

[0017] To adjust the speed of the addition reaction, the composition may incorporate addition-reaction inhibitors, such as 3-methyl-1-butyne-3-ol, 3,5-dimethyl-1-hexyne-3-ol, phenyl butynol, or a similar alkyne alcohol; 3-methyl-3-penten-1-yne,  
35 3,5-dimethyl-3-hexen-1-yne, or a similar enyne compound; 1,3,5,7-tetramethyl-1,3,5,7-tetravinyl cyclotetrasiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahexenyl



5 cyclotetrasiloxane, benzotriazole, or the like. It is recommended to use the  
aforementioned addition-reaction inhibitors in the amount of 0.0001 to 5 parts by  
weight for each 100 parts by weight of component (a).

[0018] An adhesion imparting agent can be added for imparting adhesive properties  
to the composition. Although there are no special restrictions with regard to the  
10 aforementioned adhesion imparting agent, it is recommended to use for this purpose an  
organopolysiloxane having in one molecule at least one silicon-bonded alkenyl group or  
a hydrogen atom, and at least one silicon-bonded alkoxy group. The aforementioned  
organopolysiloxane may have a linear, partially branched linear, branched, cyclic, or  
net-like molecular structure. The silicon-bonded alkenyl group can be represented by  
15 a vinyl group, allyl group, butenyl group, pentenyl group, and hexenyl group, of which  
the vinyl group is the most preferable. The silicon-bonded alkoxy group can be  
represented by methoxy group, ethoxy group, propoxy group, butoxy group, and  
methoxyethoxy group, of which the methoxy group is the most preferable. The  
silicon-bonded groups other than alkenyl groups, hydrogen atoms, and alkoxy groups  
20 may be represented by a monovalent unsubstituted hydrocarbon group such as methyl  
group, ethyl group, propyl group, butyl group, pentyl group, hexyl group, heptyl group,  
or a similar alkyl group; phenyl group, tolyl group, xylyl group, naphthyl group, or a  
similar aryl group; benzyl group, phenethyl group, or a similar aralkyl group; a  
monovalent substituted hydrocarbon group such as chloromethyl group, 3-chloropropyl  
25 group, 3,3,3-trifluoropropyl group, or a similar halogenated alkyl group; 3-  
glycidoxypentyl group, 4-glycidoxybutyl group, or a similar glycidoxyalkyl group, 2-  
(3,4-epoxychlorohexyl) ethyl group, 3-(3,4-epoxycyclohexyl) propyl group, or a similar  
epoxy-containing monovalent organic group; 4-oxylanylbutoyl group, 8-oxylanyloctyl  
group, or a similar oxylanylalkyl group. The most preferable among the above is the  
30 epoxy-containing monovalent organic group, as it imparts good adhesive properties to  
various substrates. The aforementioned organopolysiloxane is a low-viscous liquid  
substance, which at 25°C has a viscosity within the range of 1 to 500 mPa·s.

[0019] An addition reaction is carried out at room temperature or with heating.  
The speed of the reaction is higher when it proceeds with heating. It is recommended  
35 to carry out heating at a temperature of 50 to 250°C, preferably 80 to 200°C.

5 [0020] As component (B) used in the composition of the invention is characterized  
by an increased thermal conductivity, the composition can be compounded with a  
reduced amount of a thermoconductive filler (C). Since prior to thermal elongation,  
the particles of component (B) are small in shape, the composition of the invention has  
excellent flowability, is easy to handle, and is suitable for use under industrial  
10 conditions. Therefore, the composition may find application in the manufacture of  
adhesives, potting agents, and protective coatings for parts and units of electrical and  
electronic devices. In particular, the composition of the invention is suitable for use as  
a coating agent and adhesive for semiconductor devices, such as semiconductor  
elements and heat dissipation fins.

15 [0021] The following is a detailed description of a semiconductor device produced  
by using the composition of this invention. A semiconductor device of this invention  
comprises a semiconductor element attached to a substrate, or coated, by means of a  
thermoconductive liquid polymer composition of the invention. Since a cured body  
produced from the composition of the invention has improved thermal conductivity and  
20 adhesion to a substrate, the device will be characterized by improved heat dissipation  
properties and reliability. Semiconductor devices of the present invention may  
comprise diodes, transistors, thyristors, monolithic IC, hybrid IC, LSI, and VLSI.  
Semiconductor elements of the invention may comprise diodes, transistors, thyristors,  
monolithic IC, and semiconductor elements of hybrid IC's.

25 [0022] An example of a semiconductor device of the invention is an LSI, the cross-  
section of which is shown in Fig. 1. The device consists of a semiconductor element 1  
supported by a circuit substrate 2. The semiconductor element 1 and a circuit pattern  
element 3 connected to an external lead wire are electrically connected by means of a  
bonding wire 4. The surface of the semiconductor element 1 supports a  
30 thermoconductive curable liquid polymer composition 5 of this invention, which  
functions as a protective layer for the semiconductor element and as an adhesive agent  
for heat dissipation fins 6. The circuit substrate 2 can be made from a glass-fiber  
reinforced epoxy resin, bakelite resin, phenol resin, or a similar organic resin; alumina  
or a similar ceramic; copper, aluminum, or another metal. The circuit pattern element  
35 3 may be made from copper or silver-palladium. Typical materials of the bonding wire  
4 are gold, copper, and aluminum. Heat dissipation fins 6 are produced from

5 aluminum, copper, nickel, or the like. In addition to semiconductor element 1, the circuit substrate 2 may support other electronic parts such as resistors, capacitors, coils, etc.

[0023] In the manufacture of the semiconductor device of the invention, first the semiconductor element 1 is placed onto the circuit substrate 2, the semiconductor  
10 element 1 and the circuit pattern element 3 are electrically interconnected by means of the bonding wire 4, the thermoconductive curable liquid polymer composition 5 is applied onto the surface of the semiconductor element 1, and the plate with heat dissipation fins 6 is attached to the device. The entire unit is then heated to a temperature of 50 to 200°C and, as a result, the semiconductor element 1 and the heat  
15 dissipation fins 6 are fixed in place.

#### EXAMPLES

[0024] In the following examples, all viscosities are measured at 25°C. Thermal conductivity, hardness, and reliability were evaluated by the methods described below.

#### 20 Method for Evaluating Thermal Conductivity of the Cured Body

[0025] The thermal conductivity of the thermoconductive curable liquid polymer composition was measured on a (15cm long x 6 cm wide x 2 cm thick) cured body sample using a Quick Thermal Conductivity Meter, Model QTM-500, available from Kyoto Electronics Manufacturing Co., Ltd.

25

#### Method for Evaluating Hardness of the Cured Body

[0026] The hardness of the cured product of the thermoconductive curable liquid polymer composition was measured using a Type A durometer as specified in JIS K 6253.

#### 30 Method for Evaluating Reliability of the Semiconductor Device

[0027] A semiconductor device of the type shown in Fig. 1 was produced by placing a semiconductor element 1 onto a circuit substrate 2 made from a glass-fiber-reinforced epoxy resin and supporting external lead wires attached to the terminal portion, and a circuit pattern element 3 printed on the substrate surface. The circuit  
35 pattern element 3 was then electrically connected to the electronic element 1 by a bonding wire 4. After the surface of the electronic element was coated with the

5 thermoconductive curable liquid polymer composition 5 supplied from a dispenser, a plate 6 with aluminum heat dissipation fins was glued to the aforementioned surface, and the entire unit was heated at 150°C in a hot-air-circulation oven, whereby the heat-dissipation fins 6 was fixed to the semiconductor element 1. Twenty semiconductor devices were produced by this method.

10 [0028] Each semiconductor device was subjected to thermal cycle testing with one cycle consisting of holding for 30 minutes at -65°C and for 30 minutes at +150°C. Defects were determined by observing conditions of the cured composition between the semiconductor element 1 and the heat dissipation fins 6 under a microscope after 1,000 cycles. The samples did not pass the test if, after the test, the semiconductor 1 and the

15 heat dissipation fins 6 were separated. The defect rate was determined from the number of devices that did not pass the test.

#### Reference Example 1

[0029] The linear shape of a 80 µm-diameter, 4 mm-long Cu-Zn-Al shape-memory alloy wire (from Nippon Tungsten Co, Ltd.) was memorized by quickly cooling after

20 heating for 1 hour at 300°C. The wire was then wound around a rod to shape a Cu-Zn-Al memory alloy wire in the form of a coil. The core of the obtained coil-type shape-memory alloy had a diameter of 0.55 mm and a length of 0.55 mm. The transition point temperature was 120°C.

#### Practical Example 1

25 [0030] A mixture was prepared from 100 parts by weight of a 2000 mPa·s viscosity bisphenol-type epoxy resin having epoxy-equivalent quantity of 165 g; product of Tohto Kasei Co., Ltd., trademark ZX-1059; and 65 parts by weight of a diphenyldihydroxysilane which is solid at room temperature and has hydroxy-equivalent quantity of 108 grams (g). The mixture was melted by heating at 120°C.

30 After cooling to room temperature, the product was mixed with a 1100 parts by weight of a 200 mPa·s viscosity copolymer of a dimethylsiloxane and a diphenylsiloxane having both molecular terminals capped with a trimethylsiloxy and 1.0 part by weight of an aluminum tris(acetylacetonate). The components were uniformly mixed, and 800 mPa·s viscosity curable epoxy resin composition was obtained. One hundred parts by

35 weight of the obtained epoxy resin composition were combined with 600 parts by weight of 10 µm average diameter alumina spherical particles (trademark "Admafine

5 Alumina" produced by Admatex Co., Ltd.), and 10 parts by weight of the coil-shaped Cu-Zn-Al shape memory alloy obtained in Reference Example 1. After the components were uniformly mixed at room temperature, a 65 Pa·s viscosity thermoconductive curable liquid epoxy resin composition was obtained.

[0031] A cured body was produced from the obtained thermoconductive curable  
10 liquid epoxy resin composition by heating for 3 hours at 150°C. By the methods specified above, the cured body produced from the aforementioned composition was evaluated with regard to thermal conductivity and hardness, while the semiconductor device manufactured with the composition was evaluated with regard to reliability. The results of the evaluation are shown in Table 1.

15 Comparative Example 1

[0032] A 66 Pa·s viscosity curable liquid epoxy resin composition was obtained by the same method as in Practical Example 1, with the exception that 10 parts by weight of 10 μm average diameter alumina spherical particles were used instead of 10 parts by weight of the coil-shaped Cu-Zn-Al shape memory alloy.

20 [0033] A cured body was produced from the obtained thermoconductive curable liquid epoxy resin composition by heating for 3 hours at 150°C. By the methods specified above, the cured body produced from the aforementioned composition was evaluated with regard to thermal conductivity and hardness, while the semiconductor device manufactured with the composition was evaluated with regard to reliability.

25 The results of the evaluation are shown in Table 1.

Practical Example 2

[0034] A mixture was prepared from 100 parts by weight of a 2000 mPa·s viscosity dimethylpolysiloxane having both molecular terminals capped with dimethylvinylsiloxy groups (0.24 wt.% content of the vinyl groups), 0.6 parts by weight of 20 mPa·s  
30 viscosity copolymer of a methylhydrogensiloxane and a dimethylsiloxane having both molecular terminals capped with trimethylsiloxy groups (0.75 wt.% content of silicon-bonded hydrogen atoms), and a platinum-1,3—divinyl-1,1,3,3-tetramethyldisiloxane complex (5 ppm content of metallic platinum in the composition in weight units). The components were combined and uniformly mixed  
35 with 600 parts by weight of the spherical alumina particles used in Practical Example 1 and 0.01 parts by weight of an addition-reaction inhibitor in the form of a 3-phenyl-1-

5 buten-3-ol. The mixture was additionally combined and uniformly mixed at room temperature with 10 parts by weight of the coil-shaped Cu-Zn-Al shape memory alloy obtained in Reference Example 1. As a result, a 72 Pa·s viscosity thermoconductive curable liquid silicone composition was prepared.

[0035] A cured body was produced from the thermoconductive curable liquid  
10 silicone composition by heating for 1 hour at 150°C. By the methods specified above, the cured body produced from the aforementioned composition was evaluated with regard to thermal conductivity and hardness, while the semiconductor device manufactured with the composition was evaluated with regard to reliability. The results of the evaluation are shown in Table 1.

15 **Comparative Example 2**

[0036] A 74 Pa·s viscosity curable liquid silicone composition was obtained by the same method as in Practical Example 2, with the exception that 10 parts by weight of alumina spherical particles were used instead of 10 parts by weight of the coil-shaped Cu-Zn-Al shape memory alloy.

20 [0037] A cured body was produced from the thermoconductive curable liquid silicone composition by heating for 1 hour at 150°C. By the methods specified above, the cured body produced from the aforementioned composition was evaluated with regard to thermal conductivity and hardness, while the semiconductor device manufactured with the composition was evaluated with regard to reliability. The  
25 results of the evaluation are shown in Table 1.

**Comparative Example 3**

[0038] A 345 Pa·s viscosity curable liquid silicone composition was obtained by the same method as in Practical Example 2, with the exception that 180 parts by weight of alumina spherical particles of Practical Example 1 were used instead of 10 parts by  
30 weight of the coil-shaped Cu-Zn-Al shape memory alloy.

A cured body was produced from the curable liquid silicone composition by heating for 1 hour at 150°C. By the same methods as specified above for the composition of Practical Example 2, the cured body produced from the composition of this comparative example was evaluated with regard to thermal conductivity and hardness, while the  
35 semiconductor device manufactured with the composition was evaluated with regard to reliability. The results of the evaluation are shown in Table 1. Comparison showed

5 that the composition of this comparative example was more difficult to spread than the composition of Practical Example 2. Therefore it was less suitable for industrial production of semiconductor devices than the composition of the invention.

Table 1

	Practical Examples		Comparative Examples		
	1	2	1	2	3
Thermal conductivity (W/m·K)	1.7	1.7	1.4	1.4	1.7
Hardness	0	0	0	0	35
Number of semiconductor devices that did not pass reliability test (%)	0	0	0	0	10

10

#### Industrial Applicability

[0039] As the thermoconductive curable liquid polymer composition of the invention possesses flowability prior to curing, it provides excellent conditions for manufacturing under industrial conditions. The composition may find application in the manufacture of adhesives, potting agents, and protective coatings for parts and units of electrical and electronic devices. In particular, the composition of the invention is suitable for use as a coating agent and adhesive for semiconductor devices, such as semiconductor elements and heat dissipation fins.

20 [0040] A cured body formed from the composition after curing is characterized by high thermal conductivity. Furthermore, semiconductor devices of the present invention, which are assembled from semiconductor elements attached or coated with the aforementioned thermoconductive curable liquid polymer composition are characterized by improved reliability. Semiconductor devices of this invention may comprise diodes, transistors, thyristors, monolithic IC, hybrid IC, LSI, and VLSI. Semiconductor elements of the invention may comprise diodes, transistors, thyristors, monolithic IC, and semiconductor elements of hybrid IC's.

25